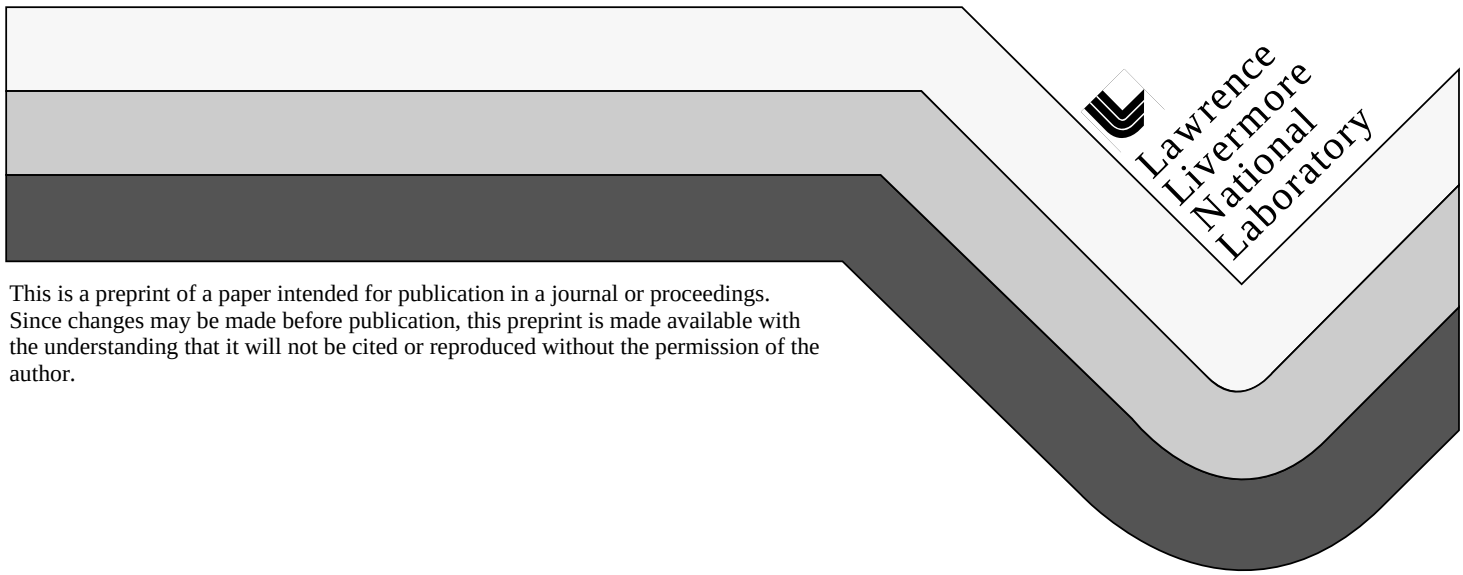
UCRL-JC-126784
PREPRINT

Aerogels-A New Material for Emissive Display Applications

S. Glauser
H.W.H. Lee

This paper was prepared for submittal to the
Society for Information Display
Boston, MA
May 11-16, 1997

March 1997



Aerogels – A New Material for Emissive Display Applications

Sally A. C. Glauser[1] and Howard W. H. Lee[2]
[1]University of California at Davis, Livermore, CA
[2]Lawrence Livermore National Laboratory, Livermore, CA

Abstract

The remarkable optical and electronic properties of doped and undoped silica aerogels establish their utility as unique, multifunctional host materials for fluorescent dyes and other luminescent materials for display and imaging applications. We present results on the photoluminescence and absorption of undoped silica aerogels and aerogels doped with Er^{3+}, rhodamine 6G (R6G), and fluorescein. We also demonstrate evidence of Fowler-Nordheim tunneling of electrons in aerogels.

Introduction

Aerogels represent a novel class of open-cell nanoporous materials with remarkable optical, electronic, thermal, and structural properties. Many of these properties are ideal for host matrices in which luminescent materials are incorporated for flat panel display (FPD) applications. Some of these properties include low weight, minimal optical and electronic interaction with the chromophore, favorable electron transport properties, and physical robustness. We investigated the optical properties of silica aerogels doped with a variety of luminescent materials including Er^{3+}, rhodamine 6G (R6G), and fluorescein. We studied the photoluminescence (PL) and absorption spectra, the photoluminescence excitation spectra, and the photoluminescence decay of these doped aerogels, and evaluated their performance for FPD purposes. We present the results on the PL and absorption. We contrast the optical properties of these doped aerogels with those observed for each chromophore and find that silica aerogels serve as ideal host matrices. We will also present results on the current-voltage (I-V) characteristics of low density silica aerogels to evaluate their potential performance in electroluminescent devices. We find evidence for Fowler-Nordheim tunneling of electrons in the aerogel matrix. We also demonstrate the attractive phenomenon of electron multiplication in silica aerogels, which we interpret as arising from the microscopic structure of aerogels. This property uniquely affords aerogels the potential for efficient and bright electroluminescence. Our results demonstrate the utility of these silica aerogels as unique, multifunctional host materials for fluorescent dyes and other luminescent materials for display and imaging applications.

Experimental

The preparation of the aerogels studied in this paper is discussed in detail in reference 1.

Transmission and absorption spectra were recorded with an absorption spectrophotometer. Optical excitation for PL studies was provided by three sources: (1) the ~100 fs output from a self-modelocked Ti:sapphire laser was frequency-doubled with an appropriate KDP crystal to give excitation pulses varying from 355-400 nm and at a 82 MHz repetition rate, (2) the ~150 fs output from a Ti:sapphire regenerative amplifier was frequency-doubled to give 400 nm excitation pulses at a 1 kHz repetition rate, and (3) a commercial fluorimeter. Photoluminescence spectra were recorded with a fluorimeter and also with a 0.25 m monochromator equipped with an intensified optical multichannel analyzer. The PL spectra were corrected for the spectral response of the optical system.

Current-voltage measurements were performed in vacuum (10^{-7} torr) with thin gold films (100-150 nm) serving as the electrodes.

Results

Figure 1 shows the PL spectrum for a typical low density silica aerogel excited at 264 nm.

This spectrum can be compared with figures 2-4, which show the photoluminescence spectra for the chromophore-doped silica aerogels.

Absorption spectra are shown in figures 5-8 for undoped aerogel, R6G in aerogel, fluorescein in aerogel, and Er^{3+} in aerogel.

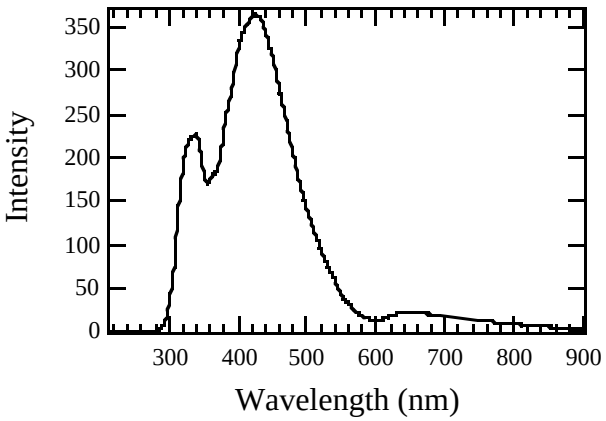


Figure 1. PL spectrum of a 30 mg/cc low density silica aerogel excited at 264 nm.

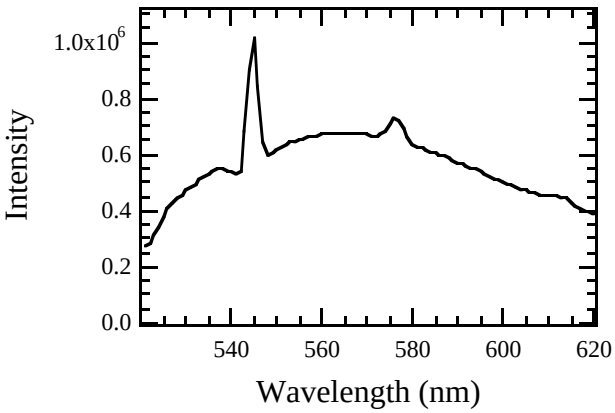


Figure 4. PL spectrum of Er^{3+} in silica aerogel excited at 450 nm.

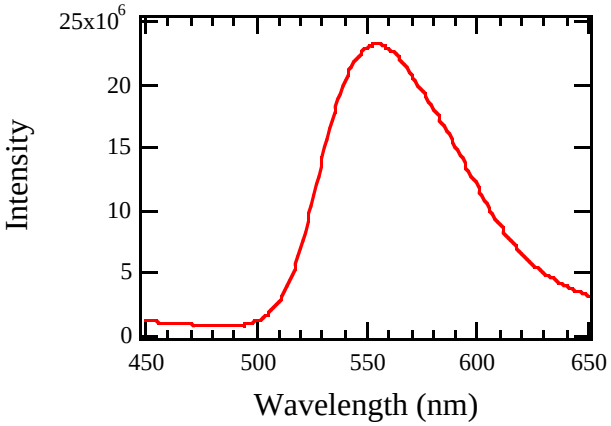


Figure 2. PL spectrum of R6G in silica aerogel excited at 365 nm.

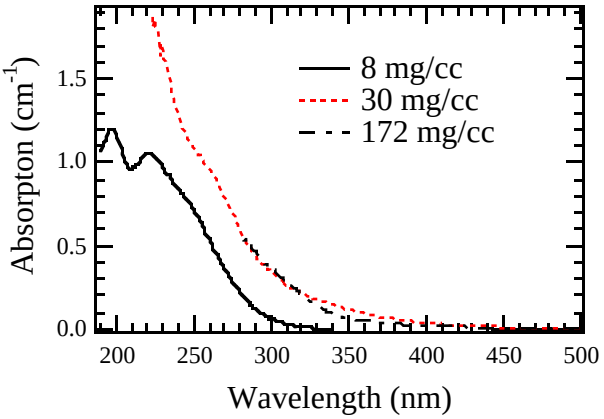


Figure 5. Absorption for different low densities of silica aerogels.

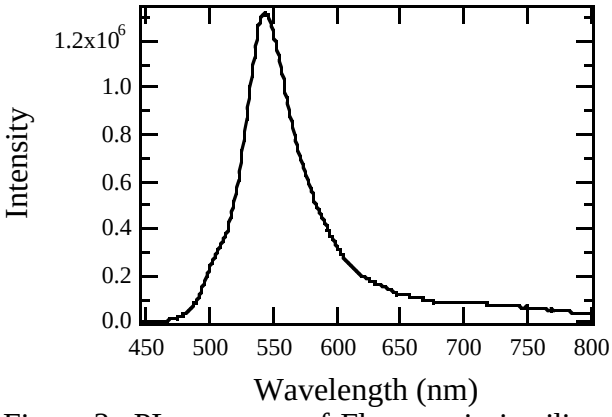


Figure 3. PL spectrum of Fluorescein in silica aerogel excited at 266 nm.

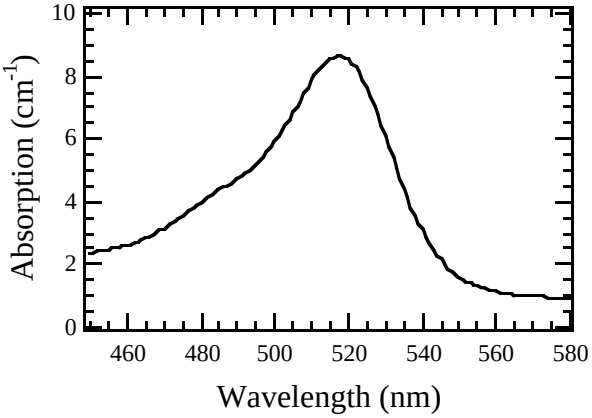


Figure 6. Absorption spectrum of R6G in silica aerogel.

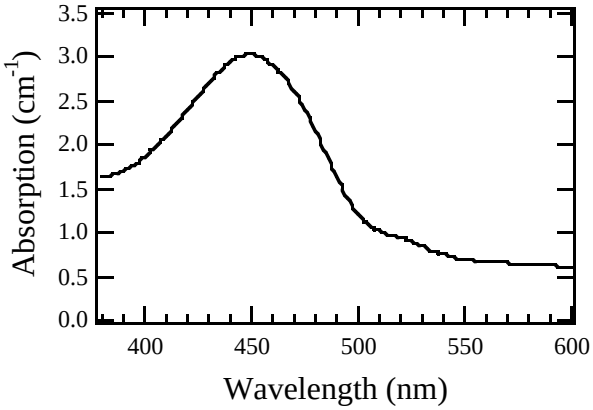


Figure 7. Absorption spectrum of Fluorescein in silica aerogel.

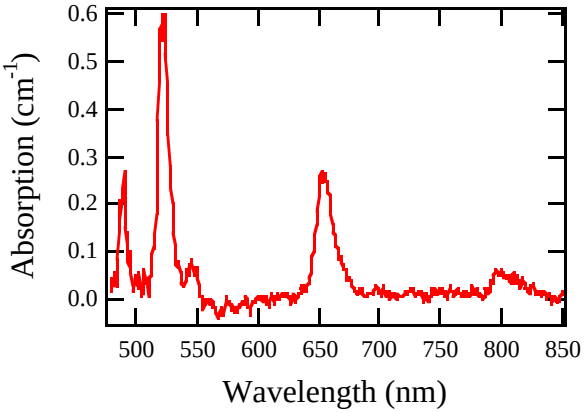


Figure 8. Absorption spectrum of Er^{3+} in silica aerogel.

Current-voltage measurements were performed on three systems: low density undoped silica aerogel, gold electrodes, and 1 pF and 12 pF capacitors. The aerogel samples were 1 mm thick and were coated with 150 nm thick gold circular pads for electrodes. The gold electrodes were also studied without aerogel at 1 mm spacing. The gold electrodes and the two capacitors were used to verify the measurements made with the aerogel. Figure 9 shows the data from the I-V measurements for the low density aerogel. The samples consistently show nonlinear increase of current with increasing voltage, with the current increasing from the pA range to the μA range as the voltage is increased. In contrast, the gold electrodes show no consistent nonlinear increase in current. The current remains in the pA range. The current across the 1 pF and the 12 pFcapacitors also remain in the pA range over the voltage region examined with the aerogel.

Discussion And Impact

The PL peaks in aerogel occur at 318, 428, and 620 nm. The absorption onset appears near 310 nm**.** All peaks occur well below the bandedge of amorphous silica, indicating the presence of defects or surface states within the aerogel. For example, the non-stoichiometric sub-oxide SiO_x has a smaller bandgap than SiO_2 ($E_g \geq$ 3-4 eV for $x \sim 1.4–1.6$). The aerogel spectra are easily distinguishable from and do not interfere with the chromophore spectra.

In the R6G sample, we observed a PL peak at 555 nm. This corresponds to a dimer transition in R6G with emission that is

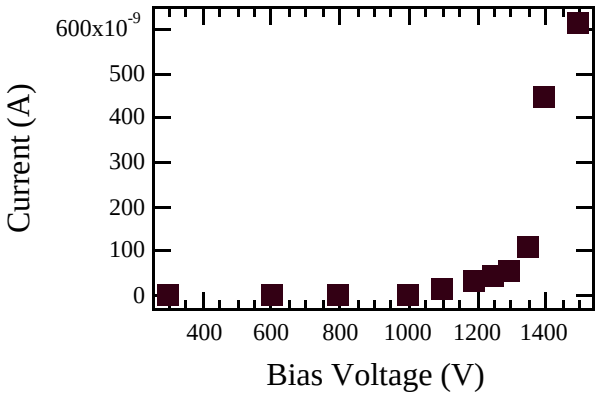


Figure 9. Current-Voltage characteristics of silica aerogel.

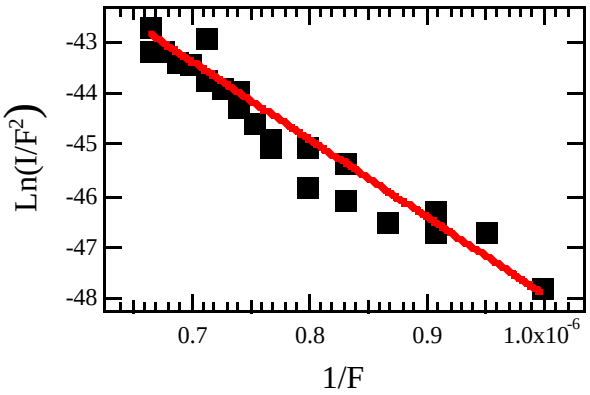


Figure 10. Fowler-Nordheim plot of electrical behavior in silica aerogel. I=current, F=electric field = Bias Voltage/distance.

reported to be between 556 - 565 nm.

Innocenzi, et. al.[2] also show a PL shoulder at 515 nm that has not been assigned. Though we do not see a luminescence peak here, we do observe a strong absorption peak near 515 nm. Our absorption spectrum also shows a shoulder at 490 nm that corresponds to the 500 nm dimer absorption of R6G.

Since the reported peak wavelength of the fluorescence of the fluorescein dimer is located at around 545 or 550 nm[3], the PL peak in our spectrum, which is observed at 544 nm, can reasonably be assigned to the dimer fluorescence. The absorption of fluorescein in methanol occurs at 498 nm which corresponds to our absorption peak.

In the Er^{3+} sample, we observe a strong Er^{3+} PL peak at 545 nm and a weaker one at 578 nm. Our absorption spectrum shows peaks at 488, 523, 545, 654, and 796 nm. In comparison, Xu, et. al.[4] reported PL peaks from Er^{3+} doped sol-gel silica glass at 525, 550, and 660 nm, which likely results from the absorption peaks we observed. The 550 nm PL is ascribed to a $^4S_{3/2}$ -> $^4I_{15/2}$ transition in Er^{3+}.

Our I-V data show a non-ohmic contact across the aerogel sample which is not present in gold-only capacitor nor the 1 pF or 12 pF capacitors. The aerogel is therefore responsible for the nonlinear I-V behavior. This nonlinearity strongly implies current amplification in the aerogel medium. There are a variety of electron conduction processes in insulators, including ionic, Schottky (thermionic) emission, space-charge limited, Frenkel-Poole emission, and Fowler-Nordheim (FN) tunneling (tunnel or field emission). A Fowler-Nordheim plot [$\ln(I/F^2)$ vs. 1/F, I=current, F=electric field] of the I-V data is shown in figure 10. This plot shows that FN tunneling may be responsible for initiating electron multiplication in aerogels.

With FN tunneling, the current density, J, is proportional to $F^2\exp(-b\phi/F)$, where F is the electric field across the sample and ϕ is the barrier height. Our data is most consistent with the Fowler-Nordheim model in the high field regime. Other processes, not discussed, appear in the low field regime and may result from thermionic emission. In addition to the method of electron transport, our data indicate that silica aerogels support electron multiplication, showing current densities as high as 10 $\mu A/cm^2$ in undoped aerogel samples. We anticipate that the appropriate dopant would significantly enhance the current amplification processes within the aerogel.

In summary, the optical and unique electronic properties of silica aerogels make them ideal hosts for fluorescent dyes and other luminescent materials for electroluminescent applications. The photoluminescence and absorption of chromophores such as rhodamine 6G, fluorescein, and Er^{3+} are not significantly altered when incorporated in an aerogel matrix. Their desirable luminescent properties (visible light emission, and high luminescent quantum efficiency) therefore remain intact. Furthermore, aerogels are unique among other host materials in providing current multiplication. Fowler-Nordheim tunneling and electron multiplication in the aerogel matrix enables bright electroluminescence at relatively low operating voltages. Thus, aerogels are a unique, multifunctional host material for a variety of chromophores with applications in the display and imaging fields.

This work was performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under contract No.W-7405-ENG-48.

References

1. T. M. Tillotson and L. W. Hrubesh, J. Non-Cryst. Solids, **145**, p. 44 (1992).

2. P. Innocenzi, H. Kozuka, and T. Yoko, J. Non-Cryst. Solids, **210**, p. 26 (1996).

3. T. Fujii, A. Ishii, and Y. Kurihara, Research on Chem. Intermediates, **19**, p. 333 (1993).

4. W. Xu, S. Dai, L. M. Toth, G. D. Del Cul, and J. R. Peterson, J. Non-Cryst. Solids, **194**, p. 235, (1996).